(19) Patent Office of the People's Republic of China (11) Publication number: CN 1110216A

(12) Invention Patent Application Publication Description
(21) Application number: 93120296.5

(51) Int. Cl[6]
B29D 7/01

(43) Publication date: October 18, 1995

(22) Application date: November 25, 1993

(71) Applicant: LONG Xuanhua
Address: Hekeda Company, inside the Zhongji Storage and Transportation Company courtyard, Buji Road, Luohu District, Shenzhen, Guangdong Province 518109
(72) Inventor: LONG Xuanhua

// B29K 33 : 04

Number of pages of Claims: Number of pages of Attached drawings:

(54) Name of invention: Special kind of unsaturated polyester molding compound and manufacturing method of same

(57) Abstract:

The special kind of unsaturated polyester molding compound and manufacturing method of same which are set forth in this invention employ a specially made solid terephthalic acid-type IP resin, allocated with a heterocyclic dual-bond cross-linking agent, hollow microbeads, fiber material, a peroxide initiator with a half life of 1 minute and a decomposition temperature of > 170°C, a filler, a releasing agent, a coloring agent, and the like, which undergo the processes of mixing and plasticization, formation into pellets (slab stock), and the like, to be formed into the special unsaturated polyester molding compound of this invention. This invention has advantageous arcing resistance, a high degree of heat resistance, radiation resistance, and a long shelf-life at room temperature; the features of stable product dimensions and long use life make it suitable for use in parts, arc shields, anti-radiation devices, hulls, and the like applications for aviation, space, vessels, automobiles, and electronic equipment, and the like.

A special kind of unsaturated polyester molding compound and manufacturing method of same, formed by means of raw materials composed of specially made crystallized solid terephthalic acid-type unsaturated resin, an accelerator, and modified material that undergo the three processes of mixing, plasticizing, and the production of pellets (slab stock), is characterized in that:

1. The crystallized fully solid terephthalic acid-type UP resin used in the composition and having an acid value of ≤ 25 mg KOH/g is from between 5 to 70% of the composition (ratio of weight to area, same below); the accelerator used in the composition and comprising a dual-bond heterocyclic cross-linking agent is from between 0.1 to 10% of the composition; a peroxide initiator having a half life of 1 minute and a decomposition temperature of ≥ 170°C is from between 0.01 to 5% of the composition; granules with good flow properties, a high degree of heat resistance, excellent dielectric properties, and having < 40% unbroken granules at a hydrostatic pressure of 10 MPa are from between 0 to 50% of the composition; alkali-free fiberglass, polyimide-type fiber, terylene fiber, boron fiber, and the like reinforcing materials, fiberglass cloth made of the said fiber, or high tensile strength steel wire containing lead or steel wire cloth having a diameter of < 100 UM is from between 5 to 70% of the composition; methyl butenoic acid lead, polyimide-type resin, fluoroplastic, amino plastic, or the like modified material is from between 0 to 50% of the composition; an aromatic halide-type flame retardant, inorganic flame retardant, or an imide or cyanamide halide-containing flame retardant is from between 10 to 50% of the composition; a fatty acid-type or metal soap-type silicon oil-type releasing agent is from between 0.1 to 3% of the composition; a coloring agent is from between 0 to 0.1% of the composition; and talcum powder, $CaCo_3$, or the like inorganic filler is from between 10 to 60% of the composition. The raw materials are measured and compounded in accordance with the above requirements, mixed at a temperature of ≤ 80°C, plasticized at a temperature range lower than 20°C, the decomposition temperature at which the hardener that is being used has a half life of 10 hours, and a molding compound in pellets or a molding compound in slabs is produced.

Special kind of unsaturated polyester molding compound and manufacturing method of same

This invention pertains to a special kind of unsaturated polyester molding compound and manufacturing method of same.

In the past, unsaturated polyester molding compounds primarily employed liquid unsaturated polyester together with fiberglass, inorganic filler, an alkene-type or propionic acid-type monomer linking agent, an initiator, a releasing agent, a coloring agent, and the like raw materials, which were blended or milled and pulverized to form a paste and fiberglass press molding compound (PMC), sheet molding compound (SMC), bulk molding compound (BMC), or granular material, and the like, which have been widely used in aviation, vessels, automobiles, electronic equipment, machine bed electrical equipment, and the like areas. Their energy-saving and anti-clustering effects have attracted attention; however existing unsaturated polyester molding compounds still exhibit such disadvantages as having a narrow applicable range with respect to forming and manufacturing, poor usage organization, high specific gravity, relatively poor dielectric properties and arcing resistance, unstable dimensions, relatively poor heat [resistance], short [use] life, and the like. For example, Japanese patent "Authorized publication (B2) H2-38086 Thermosetting resin forming compound," which employs a liquid unsaturated polyester resin and an alkene-type cross-linking agent, hollow microbeads, fiberglass, filler, and the like, which are plasticized and formed into slabs or logs of forming compound using an extruder, is only suitable for compression molding or plunger-driven injection forming compound, having a short shelf-life and a narrow applicable scope; also, for example, the VYLOGLAS UP product series manufactured by the (Japan) Toshiba Chemical Product Company, a BMC to which fiberglass has been added and that is only suitable for die-casting, plunger-driven injection molding, and forming by means of a turning screw using AP 301BG material, has a high specific gravity (from 2 to 2.1 g/cm^3), low arcing resistance, poor impact strength, and a high rate of contraction during forming; also, for example, UP-100 dry type unsaturated polyester molding compound produced by Guilin Electronic Scientific Research Institute, which is in powdered form, and, as everyone knows, powdered compound is difficult to feed when using turning screw injection molding and has to be added and stirred by hand, using a small spoon, and hence is not suitable for automated mass production, and moreover products made therefrom have a high specific gravity, a high rate of contraction, poor heat resistance, and average electrical performance; and so, to sum up, existing unsaturated polyester molding compounds have a single function, narrow applicable scope, poor technical indexes, and involve relatively simple production methods.

The goal of the present invention is to provide the public with a special kind of unsaturated polyester molding compound and manufacturing method of same that overcomes the disadvantages of the abovementioned unsaturated polyester molding compounds and manufacturing methods and that has excellent special characteristics, light specific gravity, excellent forming and manufacturing performance, and a long shelf-life.

The present invention is realized by means of the following plan:

In order to solve the problems associated with existing unsaturated polyester molding compounds and manufacturing methods, the present inventor has performed many years of research and, through the rational selection and production of raw materials for synthesizing unsaturated polyester, has combined the unsaturated polyester (UP) produced thereby with an optimally selected cross-linking agent, initiator, reinforcing filler, hollow microbeads, flame retardant, modified material, releasing agent, coloring agent, and the like raw materials, and, using an advanced, improved method, has mixed and plasticized these materials and formed granules (slab stock), forming a special unsaturated polyester molding compound. For a schematic diagram of the production process, see Figure 1.

The unsaturated polyester resin used in this invention, a solid terephthalic acid-type unsaturated polyester, employs purified terephthalic acid (PTA), dimethyl terephthalate (DMT), 1,4-butanediol (BD), maleic anhydride (MA), bis-2-hydroxyethyl terephthalate (BHET), bis-2-hydroxybutyl terephthalate, and the like raw materials; and is formed through the coordination of a zinc acetate or acetic acid catalyst; Sb_2O_3 or [$Ti(OC_4H_9)$] as a polymerization inhibitor; hydroquinone with a substituted [p-phenylphenol] or substituted hydrazine ring; and the like raw materials. See figure drawing for manufacturing process flow chart; that is, this invention uses PTA and EG or DMT and EG (BD) to perform esterification or an ester-exchange reaction, and the bis-2-hydroxyethyl terephthalate or bis-2-hydroxybutyl terephthalate and the MA generated by the reaction undergo polycondensation in the presence of the polymerization inhibiting agent, thereby forming solid UP. The foregoing processes for producing UP are performed under special technical conditions (see Figure 1). Obviously, the molecules of the solid UP resin manufactured using the abovementioned raw materials contain aromatic cores with excellent symmetry at the para position, therefore ensuring that the special unsaturated polyester molding compound of the present invention has excellent chemical stability and heat resistance.

The UP resin produced in this invention is pulverized to form granules of from 0.1 to 1000 um and is mixed with one or several of the following specially chosen accelerators or modified materials. For the allocated amounts, see Table 2.

Cross-linking agent: maleimide, M-type monomer, melamine, triallyl cyanurate, polyamide-amic acid, low molecular weight polyimide, polyamic acid, phenyl maleimide, N,N′-meta-phenylene-bis-maleimide, N,N′-ethylene-bis-maleimide, diallyl phthalate, methyl butenoic acid lead. The heterocyclic double bonds in these compounds endow the special unsaturated polyester molding compound of the

present invention with special properties, namely, the special unsaturated polyester molding compound has increased heat resistance and strength,'and improved chemical resistance, radiation resistance, and durability.

Blending of reinforcing material: alkali-free fiberglass, polyimide fiberglass, polyacrylonitrile-based carbon fiber, polytrifluorochloroethylene fiber, alumina fiber, terylene fiber, fire-retardant terylene fiber, boron fiber, glass microbeads, and fiberglass cloth from the foregoing fiber. High tensile strength steel wire and steel wire cloth containing lead and having a diameter of [< 100 UM].

Blending of modified material: polytetrafluoroethylene, fluoroplastic 40 poly-bis-maleimide, polyimide, melamine formaldehyde molding powder, polyester-imide, polyphenyl ether, polyphenyl, polyamide-imide, and polyetherimide.

Filler: the properties required for hollow microbeads: at a hydrostatic pressure of 10 MPa/ cm^2, the percentage (by volume) of unbroken granules is < 40%; true specific gravity is 0.15 to 0.70 grams/cm^3; average granule diameter is from 30 to 80 microns; surfaces are smooth; and heat resistance and electrical insulation properties are excellent. Primarily, hollow glass microbeads, hollow ceramic microbeads, and the like, and hollow microbeads that meet the above performance requirements are used. Other fillers that are used in association therewith: lightweight calcium carbonate, talcum powder, $CaSo_4$, and $BaSo_4$ clay.

Flame retardant: aluminum hydroxide, polytetrafluoroethylene, tetrabromo-bisphenol A glycidyl ether, zinc borate, hexabromobenzene, antimony trioxide, tetrabromo-bisphenol A, tris (2,3 – dibromopropyl) isocyanurate, bis-tetrabromo-phthalimide, tetrabromo-bisphenol A (2,3 – dibromopropyl) ether, dibromomethyl glycidyl ether, benzoguanamine, tetrabromo-bisphenol A (allyl) ether, and 1,2-bis-(2,4 –tribromophenoxy)ethane.

Initiator (hardener): dicumyl peroxide, cumyl hydroperoxide, 2,2-bis(tert-butylperoxy)diisopropyl benzene, 2,5-dimethyl-2,5(tert-butylperoxy)hexane, tert-butyl-hydroperoxide.

Releasing agent: zinc stearate, lead stearate, fatty acid amide, organic silicon oil.

Coloring agent: titanium white, oily black, iron red macromolecular pigments.

After the foregoing raw materials are allocated properly, production is performed at a temperature range less than 20°C, such that the half-life of the initiator that is used is 10 hours, and in accordance with

the technical conditions stipulated in Table 3 and the special unsaturated polyester molding compound production process flowchart.

The beneficial effects of this invention are:

The special kind of unsaturated polyester molding compound produced in this invention has the following amazing properties that previous kinds of unsaturated polyester molding compound have lacked:

1. The sizes of granules in granular raw material are mutually close, and almost no powder is present. The granules do not stick to each other. Slab stock is a solid slab.

2. Shelf-life stability is over 15 months (at 24°C).

3. Excellent injection molding (turning screw) manufacturing performance. Granules flow smoothly when charged into feed funnel and can be used for compression molding or transfer molding manufacturing.

4. Chemical properties extremely stable. Higher resistance to acid, alkali, oil and grease, and solvents than existing unsaturated polyester molding compounds.

5. Excellent arcing resistance (> 180 to 280 seconds), dielectric strength high, excellent electrical insulator.

6. Low rate of heat transfer, high degree of resistance to heat and humidity, long use life.

7. Has excellent capacity to resist radiation.

8. Specific gravity relatively light (0.8 to 1.8 g/cm^3), excellent mechanical strength.

9. Inexpensive, unusually good performance.

The special properties possessed by the special unsaturated polyester molding compound of this invention endow the series of products made therefrom and including insulating materials, temperature-preserving fire-resistant materials, anti-radiation materials, materials for durable coverings, arc shield components, hulls, and the like, in the fields of aviation, space, automobiles, vessels, and mechanical and electrical equipment fields, with excellent energy-saving effects.

Embodiment 1:

1,4-butanediol (BD), dimethyl terephthalate (DMT), maleic anhydride (MA), are allocated in a BD : DMT : MA molar ratio of 2.2 : 1 : 2. First, BD and

DMT, in accordance with the allocation ratio, undergo ester exchange reaction in the batch vessel or the continuous reaction vessel at from 160 to 210°C. The byproducts methanol and tetrahydrofuran are distilled away. When the amounts distilled away reach from 86 to 90% of the theoretical amounts thereof, the reaction is stopped. The bis-2-hydroxybutyl terephthalate that is generated thereby is pumped into a polycondensation reaction vessel that has been charged with MA weighed out in accordance with the allocation amounts and reacted under the protection of N_2 gas, at a vessel temperature of from 180 to 210°C and with the temperature at the top of the reaction equipment ranging from 160 to 190°C, for 1.5 to 2.5 hours; and then is added to a quantity of the polymerization inhibitor hydroquinone equal to 0.002% (by weight-area ratio) of the reactant and reacted at 210 to 250°C at a pressure of 133 Pa for from 4 to 6 hours; then the temperature is reduced to less than 230°C, vacuum-pressurized to from 7 to 10 kPa, and reacted for from 0.8 to 1.2 hours; then the pressure is reduced to from 4 to 7 kPa and reaction is continued for from 0.4 to 0.8 hours; then pressure is reduced to from 1 to 4 kPa and reaction is continued for from 0.2 to [0.5] hours; and finally the pressure is reduced to from 0.1 to 1 kPa and reaction is continued for from 0.1 to 0.5 hours. When acid value reaches 15 mg KOH/g, the melted UP is drawn off at a temperature of under 200°C, cooled, and the crystalline, completely solid UP resin used in this invention is obtained. During the reaction process, the BD and the small quantity of tetrahydrofuran that are boiled off are recovered through the recovery system.

The UP that has been prepared in the said manner is blended with from 0 to 10% talcum powder, pulverized to form a powder of from 0.1 to 1000 um, and then, in accordance with each of the formulations given in Table 4, using the German LEISTRIT[2] Corporation's ZSE series dual turning-screw planetary-geared pelletizer plasticizer-extruder unit or a similar dual turning-screw pelletizer-extruder unit, mixing and plasticizing are performed at a temperature range of < 105°C, and strand extrusion and hot cutting pelletizing yield the special kind of unsaturated polyester molding compound of this invention, in the form of a pelletized compound.

Embodiment 2:

PTA : EG : MA are measured out at a molar ratio of 1 : 2.1 : 2, and the continuous polyesterification polycondensation method is used to produce UP resin. For technical conditions that apply to the reaction, see Table 5.

The UP resin that is obtained in accordance with the foregoing conditions is continuously sent to the slab stock production line where it is formed into slabs of solid fiberglass cloth molding compound.

The UP resin obtained in the foregoing manner can also be continuously sent to be cooled and pulverized to form grains of from 0.1 to 1000 um. Then the UP resin powder can be formed into pellets using the method of Embodiment 1.

Embodiment 3:

UP resin powder is produced in accordance with Embodiment 1 or 2, respectively. The UP resin

powder is weighed out in coordination with each of the respective embodiment formulations in Table 3. First, the powder and liquid activator and modified material are charged into a high-speed mixer and are mixed at a temperature of < 80°C for between 2 to 5 minutes, after which alkali-free short fiberglass is added and mixed for between 2 to 5 minutes, and the thoroughly mixed material is charged into a batchwise screw feeder. At a fixed time and in a fixed amount, the screw feeder feeds the material into a dual roller mill; the material is milled at from 90 to 100°C for between 8 to 10 minutes, and then the material is discharged. The material in band form is formed into slab stock or, by means of a cutter, is formed into square pellets.

Embodiment 4:

The pellet stock obtained in the foregoing embodiment is modeled in a thermoset injection molding machine. The injection molding technical parameters are:

Feed cylinder temperature: 40 to 70°C (feed input [side]) 70 to 95°C (spray nozzle side)

Mold temperature: 170 to 220°C

Injection pressure: 5 to 8 MPa

Back pressure: 0.5 to 1 MPa

Turning screw rotating speed: 60 to 80 rpm

Time: injection forming: 1 to 5 minutes; after mold release, curing at 180 to 250°C for 0.2 to 20 hours.

In accordance with GB1141-78, test sample's arcing resistance is from 180 to 280 seconds.

In accordance with GB1140-78, test electrical insulation: electrical insulation is from 10^9 to 10^{17} (Ω).

In accordance with GB1636-79, test sample's density: density is 0.8 to 1.8 g/cm^3.

Flammability: UL94 V-O level

In accordance with GB1634-79, test that sample's heat deformation temperature is ≥ 200°C.

Figure 1: Special unsaturated polyester molding compound production process flowchart.

Figure 2: Solid terephthalate-type UP resin production process schematic diagram.

Figure 3: Special unsaturated polyester molding compound production process flowchart.

Table 1

Production method	Proportions of raw materials: Molar ratio	Catalyst	Polymerization inhibitor	Reactant	Reaction conditions: Temperature (°C)	Time hr	Pressure KPa	Equipment conditions	Other conditions	UP acid value koHmg/g
Batch ester-exchange polycondensation method	DMT : EG (BD) : MA 0.4 – 0.7 : 0.9 – 1.6 : 0.8 – 1.5	0 – 0.2	0.0005 – 0.1	DMT + EG (BD)	160 - 220	3 - 6		Ester exchange reactor		25 <
				+ MA	190 – 260 200 - 280	5 – 8 2 - 5	0.1 - 2 0.1 – 2.0	Polycondensation reactor	Input nitrogen, add hydroquinone	
Batch esterification polycondensation method	PTA : EG : MA 0.9 – 1.2 : 1.4 – 2.4 : 1.3 – 2.4			PTA EG	180 - 240	3 - 6		Esterification reactor		
				+ MA	200 – 250 210 - 280	4 – 7 3 - 6	0.1 - 3 0.1 – 2.5	Polycondensation reactor	Input nitrogen, add hydroquinone	
Continuous ester-exchange polycondensation method	DMT : EG (BD) : MA 0.4 – 0.7 : 0.8 – 1.2 : 0.8 – 1.5			DMT + EG (BD)	160 - 330	1.5 – 3.5		Number one ester exchange reactor		
					180 -240	1.5 – 3.5		Number two [ester exchange] reactor		
				+ MA	180 - 220	1.5 – 3.5	0.133	Number one polycondensation reactor	Input nitrogen	
					190 - 260	1.5 – 3.5	0.3 - 3	Number two polycondensation reactor	Add hydroquinone	
					200 - 280	1.5 – 3.5	1.5 - 11	Number three polycondensation reactor		
					210 - 280	1.5 – 3.5	0.1 – 1.5	Number four polycondensation reactor		
Continuous esterification polycondensation method	PTA : EG : MA 0.9 – 1.3 : 1 -2.6 : 1.3 – 2.5			PTA + EG:	180 - 240	1.3 – 3.8		Number one esterification reactor		
					190 - 260	1.3 – 3.8		Number two esterification reactor	Input nitrogen	
				+ MA	180 - 220	1.3 – 3.8	0.133	Number one polycondensation reactor	Add hydroquinone	
					200 - 280	1.3 – 3.8	0.5 – 3.5	Number two polycondensation reactor		
					200 - 250	1.3 – 3.8	2 - 10	Number three polycondensation reactor		
					210 - 280	1.3 – 3.8	0.1 – 1.5	Number four polycondensation reactor		

Table 2 Proportions of raw materials for special unsaturated polyester molding compound

Raw material	Nature of Material	Amount
		Weight percentage (%)
UP resin	0.1 um to 1000 um fine, crystalline powder	10 - 70
Initiator	Fine crystalline particles using dimethyl benzene blended with toluene and dissolved together with cross-linking agent	0.01 - 5
Cross-linking agent	Powder	0.1 – 10
Filler	Fine powder, granule radius ≤ 500 um	0 - 75
Reinforcing material	Long fiber, short fiber, fiberglass cloth mesh containing Pb, containing gold, steel wire ∅ ≤ 0.10 mm	5 -70
Modified compound	Fine powder	0 - 60
Fire retardant	Viscous liquid, fine powder	0 - 60
Releasing agent	Fine powder	0.1 - 3
Coloring agent	Powder ≥ 500 grade	0.001 – 0.1

Table 3 Special unsaturated polyester molding compound production process conditions

Equipment conditions	Production sequence	Key points of control		Nature of molding compound
		Temperature (°C)	Time (min)	
ZSE series extruder pelletizer production line gas-driven mixer; Baffled double-cone mixer; high-speed mixer; vibrating sieving and milling device; extruder; pelletizer; screw feeder	Weigh raw materials – mix – mill – attach strand – exhaust – extrude – position at head of mixer – hot-cut compound / cut cold strips – sieve – weigh – package	40 – 80 70 - 99	2 – 5 5 - 8	Pellets Solid
Slab molding compound production line	UP resin powder – transmission belt – block production line Fiberglass cloth Solid slab stock	105[≤]	12 <	Slab Solid
High-speed mixer Screw feeder Internal mixer; vibrating sieve; Dual-roller machine; pelletizer	Weigh – mix – add feed – plasticize Internal mixer – strand drawn by dual roller machine – long fiber attached Pelletize – sieve –package Solid slab stock	80 - 150	6 - 8	Solid

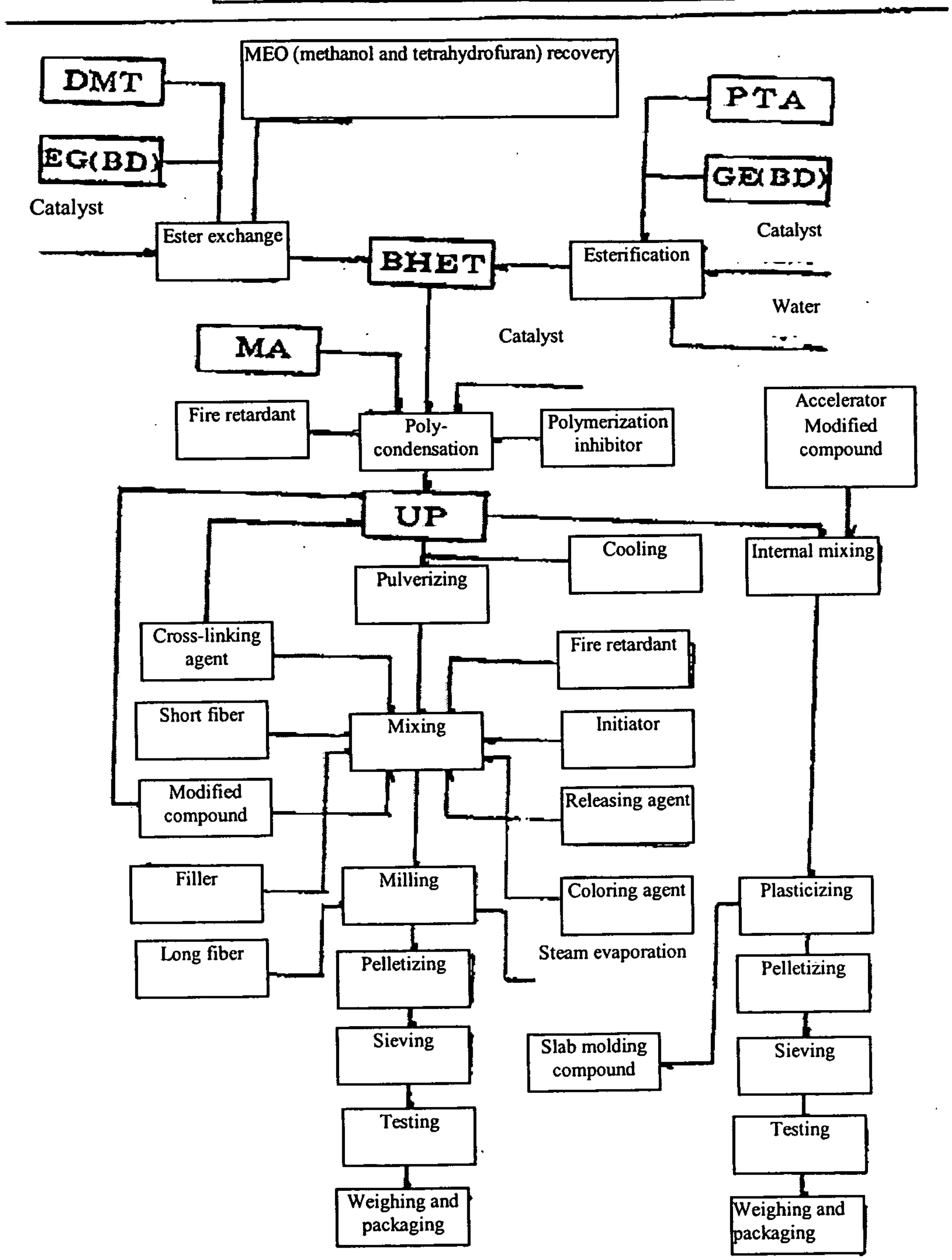
Table 4

	Embodiment								
	1	2	3	4	5	6	7	8	9
UP resin	25	25	20	23	30	28	15	32	18
Maleimide	3		4				5		
M-type monomer		4				6			
Polyamide-amic acid				1.5	2			2	0.5
Dicumyl peroxide	0.5			0.4	0.6				
Cumyl hydroperoxide		0.5	0.8			1	1	0.2	
Hollow glass microbeads	40	20	20	30	50	30	20		35
Lightweight calcium carbonate		10	13	35		8		20	10
Talcum powder	0.5								
Polytrifluorochloroethylene fiber			2						3
Alkali-free fiberglass	9	10	12	6	15	14	10	25	12
Aluminum hydroxide	10	10	15				12		6
Tetrabromo-bisphenol A				3.5					
Fluoroplastic 40	11	20					9	20	
Melamine formaldehyde molding compound									15
Fatty acid amine	1	0.5	1.2	0.6	1	1	2	0.8	0.5
Poly-bis-maleimide			10			10	26		
Polyimide fiber			2		1.4	2			

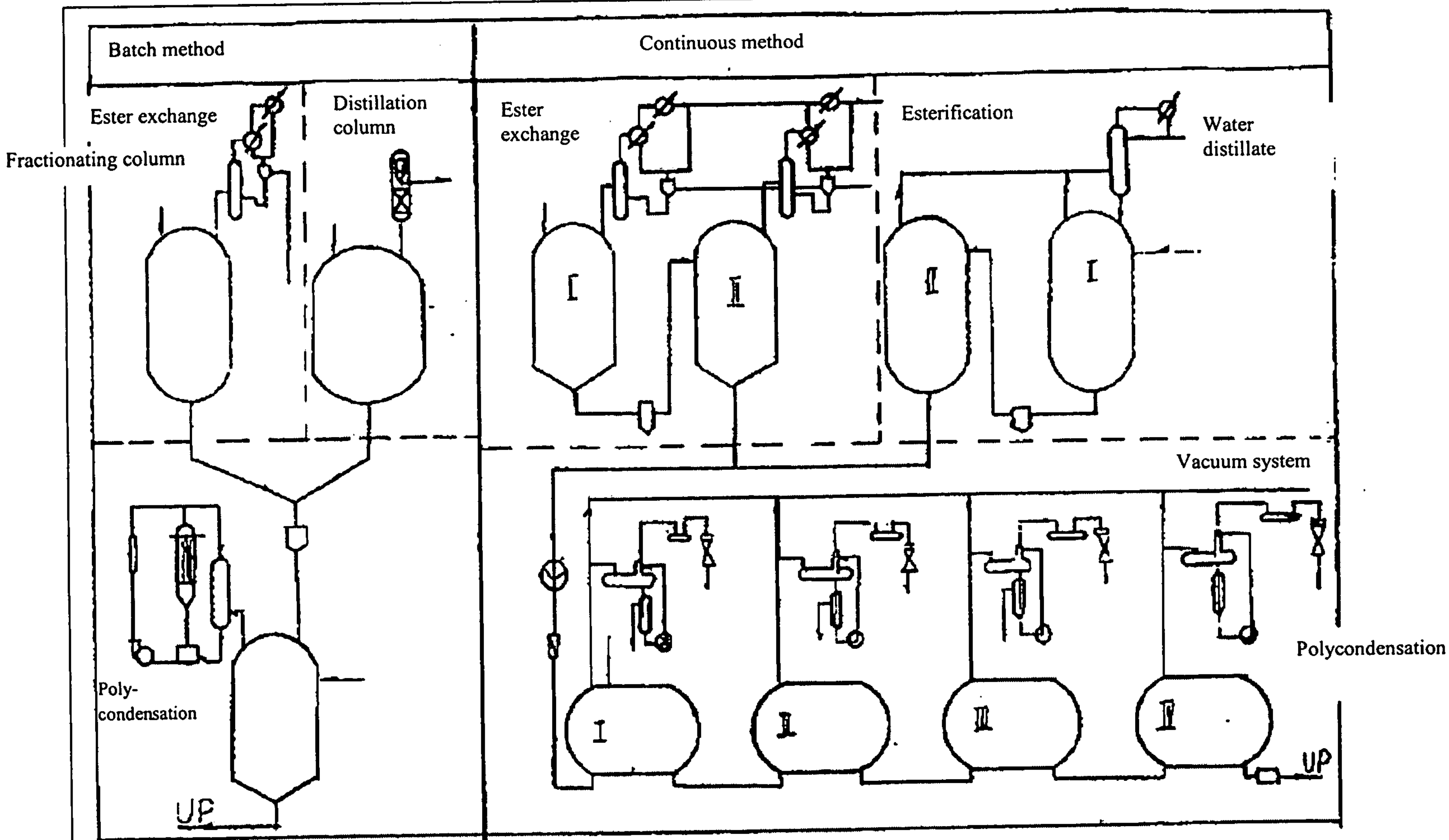
Table 5

		Reaction conditions			Other conditions
		Time (hr)	Temperature (°C)	Pressure KPa	
Polycondensation reactor	Number one esterification reactor	1.5 – 3.5	180 - 200	0.3 - 3	
	Number two esterification reactor	1.5 – 3.5	180 - 240	0.1 - 2.5	
Esterification reactor	Number one polycondensation reactor	1.3 – 2.4	200 - 220	0.133	Input nitrogen
	Number two polycondensation reactor	1.3 – 2.5	210 - 280	0.5 – 3.6	Hydroquinone
	Number three polycondensation reactor	1.4 – 2.4	220 - 240	1.5 - 11	
	Number four polycondensation reactor	1.3 – 3.8	190 - 250	0.1 - 3	

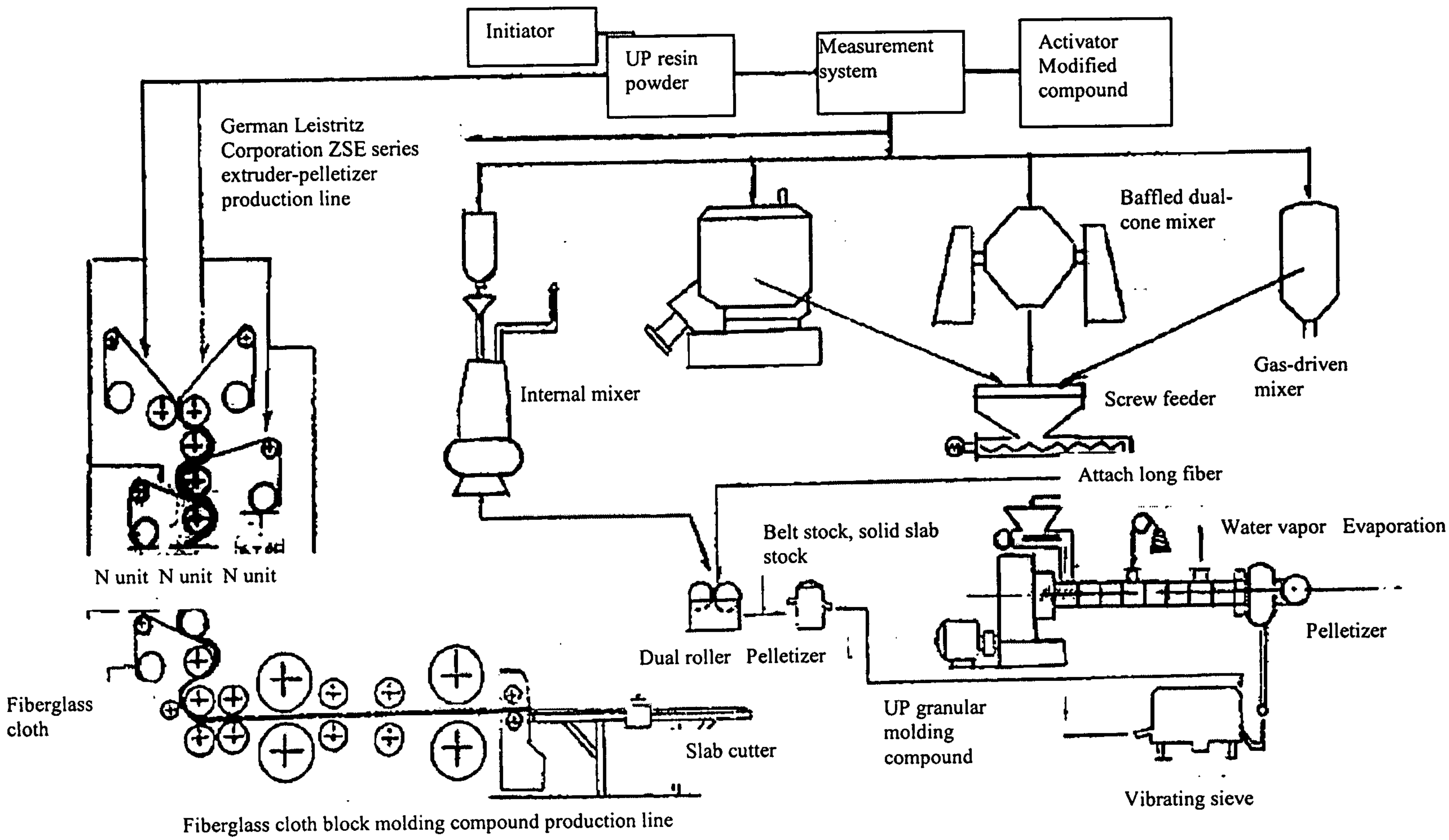
Description: Attached Drawings



[handwritten: Figure 1]



[handwritten: Figure 2]



[handwritten :Figure 3]

[19]中华人民共和国专利局

[11] 公开号 CN 1110216A

[12] 发明专利申请公开说明书

[21]申请号 93120296.5

[51]Int.Cl⁶
B29D 7/01

[43]公开日 1995年10月18日

[22]申请日 93.11.25

//B29K 33:04

[71]申请人 龙炬华
地址 518109广东省深圳罗湖区布吉路中机储运公司院内和科达公司
[72]发明人 龙炬华

说明书页数: 附图页数:

[54]发明名称 特种不饱和聚酯模塑料及其制造方法

[57]摘要

本发明的特种不饱和聚酯模塑料及其制造方法，是采用特制的固态对苯二甲酸型IP树脂，配以杂环双键交联剂，中空微球、纤维材料，1分钟半衰期分解温度>170℃的过氧化物引发剂、填料、脱模剂着色剂等，经混合、塑炼、制颗粒（板状料）等过程制成本发明的特种不饱和聚酯模塑料，本发明具有耐电弧性优、耐热温度高、耐辐射、常温贮藏期长，制品尺寸稳定，使用寿命长的特点，适合于航天、航空、船舶、汽车、电器设备等作结构件、灭弧罩、防辐射装置、壳体等。

(BJ)第1456号

权 利 要 求 书

特种不饱和聚酯模塑料及其制造方法，是将由特制的结晶全固态对苯二甲酸型不饱和树脂，助剂和改性材料组成的原料，经混合、塑炼、制颗粒（板状料）三个过程制成，其特征是：

１、组分中采用的结晶全固态对苯二甲酸型UP树脂酸值25mgKOH/g<，占组份的5-70%(重量面分比, 以下均同) 采用的助剂有含双键杂环的交联剂，占组份的0.1-10%，１分钟半衰期分解温度≥１７０℃的过氧化物引发剂，占组份的0.01-5%,流动性好，耐热温度高，价电性能优的１０MPa静水压非破坏粒子<４０%，占组份的０－５０%；无碱玻璃纤维，聚酰亚胺类纤维、涤沦纤维硼纤维等增强材料，上述纤维的纤维布，直径<100UM含铅高强度钢丝和钢丝布，占组份的５－７０%；甲基丙烯酸铅、聚酰亚胺类树脂、氟塑料、氨基塑料等改性材料，占组份的０－５０%卤素类芳族阻燃剂，无机阻燃剂，亚胺基、氰氨基含卤素阻燃剂，占组份的10-50%脂肪酸类，金属皂类硅油类脱模剂，占组份的0.1－3%，着色剂，占组份的０－０.１%，滑石粉，$CaCo_3$等无机填充剂，占组份的１０－６０%。按上述条件，计量配制的原料，在８０℃≤温度下混合、在底于所用固化剂半衰为１０小时分解温度２０℃以下的温度范围内塑炼、制颗粒状模塑料或平板状模塑料。

1002
92.2

说 明 书

特种不饱各聚酯模塑料及其制造方法

本发明涉及一种特种不饱和聚酯模塑料及其制造方法。

以往的不饱和聚酯模塑料，主要采用液态的不饱和聚酯，与玻璃纤维、无机填料、烯烃类或丙酸类单体联剂、引发剂、脱模剂、颜料等原料，经掺混或混练、粉碎，制成糊状予混玻纤团料（PMC）、片状模塑料（SMC）、料团模塑料（BMC）以及粉粒料等，在航空、船舶、汽车、电子设备、机床电器等方面广泛运用，起节能和防拥作用，受到人们的关注，然而，现有不饱和聚酯模塑料，尚存在成型加工适用范围窄、使用层次低、比重大、介电性和耐电弧性较低，尺寸不稳定，而热性较差，使用使用寿命短等弊端。如日本专利“特许公报（B2）平2－38086热硬化性树酯成型材料”采用的是液状不饱和聚酯树脂与烯烃类交联剂，中空微球、玻纤、填料等，经混炼由挤压机制出板状或柱状成型料，只适合于模压或柱塞式注射成型材料贮存期短，适用范围窄，又如（日本）东芝化学产品公司生产的=VYLOGLAS UP系列产品，玻璃纤维增加的BMC，只适合于压铸和柱塞式注射成型，螺杆成型用AP301BG料，比重大（2-2.1g/cm³），耐电弧性低、冲击强度低，成型收缩率高，再如桂林电器科学研究所制的UP－100干式不饱和聚酯模型料，为粉粒状态，众所周知在采用螺杆注射成型时，粉粒料不易下料，需人工小勺加料和捅料，不适宜于自动化大生产，制品比重大，收缩率高，耐热性差，电性能一般，总之，现有不饱和聚酯模塑料，性能单一，适用面窄，技术指标低，制法较简单。

本发明的目的，在于向公众提供一种，克服上述不饱和聚酯模塑料及制法存在的弊端的具有特性能优异、比重轻、成型加工性能优异贮藏期长的特种不饱和聚酯模塑料及其制造方法。

本发明通过下述方案实现：

本发明者为解决现有不饱和聚酯模塑料及制法存在的问题，进行了长年的研究，通过对合成不饱和聚酯原料的合理选择和制造，将制成的不饱和聚酯（UP），配以优选的交联剂，引发剂、增强填充剂、中空微球、阻燃剂、改性材料、脱模剂、着色剂等原料，采用先进完善的方法，进行混合、混炼、造粒（板状料），制成了特种不饱和聚酯模塑料，制造工艺线路图见图1。

本发明使用的不饱和聚酯树脂，为固态的对苯二甲酸型不饱和聚酯，是采用精对苯二甲酸（PTA），对苯二甲酸二甲酯（DMT）、1，4—丁二醇（BD）、顺丁烯二酸酐（MA）、对苯二甲酸双羟乙酯（BHET）、对苯二甲酸双羟丁基酯等原料，以及催化剂醋酸锌、醋酸，Sb_2O_3、$Ti(OC_4H_9)_4$和阻聚剂，对苯二酚，取代对苯醌、取代肼环等原料配合下制造而成，其制造工艺方法流程图见图工，即本发明采用PTA与EG或DMT与EG（BD）进行酯化或酯交换反应，将反应生成的对苯二甲酸双羟乙酯或对苯二甲酸双羟丁基酯与MA在阻聚剂存在下进行缩聚，制得固态的UP。上述制造UP的过程是在特定的工艺条件下完成的，见表1，显而易见，采用上述原料制造的固态UP树脂，分子中含有对称性极好的芳核对位体，因而保证了本发明的特种不饱和聚酯模塑料，具有优异的化学稳定性、耐热性。

本发明所制提的UP树脂，经粉碎制成0.1-1000um的粉粒，与下述的特选助剂和改性材料中的一种或几种进行配料，其配比量见表二。

交联剂：马来酰亚胺、M型单体、三聚氰胺、三聚氰胺三烯丙酯，聚胺一酰胺酸、低分子量聚酰亚胺、聚酰胺酸、苯基马来酰亚胺N、N'－间苯撑双马来酰亚胺，N、N'－乙撑双马来酰亚胺，苯二甲酸二烯丙酯、甲基丙烯酸铅这些化合物中，含有双键杂环，赋予本发明之特种不饱和聚

酯模塑料特殊的性能，即增加特种不饱和聚酯模塑料的耐热性和刚性，提高耐化学性、耐辐射性和耐磨性。

共混增强材料：无碱玻璃纤维、聚酰亚胺纤维、聚丙烯晴基碳纤维、聚三氟氯乙烯纤维、氧化铝纤维、涤沦纤维、阻燃涤沦纤维、硼纤维、玻璃微球。以及上述纤维的纤维布。直径100<UM含铅高强度钢丝和钢丝布。

共混改性材料：聚四氟乙烯、氟塑料40聚双马来酰亚胺、聚酰亚胺、三聚氰胺甲醛模塑粉，聚酯酰亚胺、聚苯二醚、聚苯、聚酰胺酰亚胺、聚醚酰亚胺。

填充剂：中空系更微球，性能要求：静水压在10MPa/cm²时，非坏粒子百分数(容积)<40%，真比重0.15-0.70克/厘米³，平均粒径30- 80微米，表面光滑，耐热性和电绝缘性能佳。主要采用中空破璃微球、陶瓷质中空微球等，以及达到上述性能要求的中空微球。其它协同使用的填充剂为：轻质碳酸钙、滑石粉、$CaSo_4$、陶土$BaSo_4$。

阻燃剂：氢氧化铝、聚四氟乙烯、四溴双酚A缩水甘油醚、硼酸锌、六溴苯、三氧化二锑、四溴双酚A，三（2，3一二溴丙基）异氰酸酯、双四溴酞酰亚胺，四溴双酚A（2，3一二溴丙基）醚，二溴甲基缩水甘油醚，苯代三聚氰胺、四溴双酚A（烯丙基）醚，1，2双（2，4－三溴苯氧基）乙烷。

引发（固化）剂：过氧化二异丙苯，枯基过氧化氢，2，2－双（叔丁过氧基）二异丙苯，2，5－二甲基－2，5（叔丁过氧基）已炔，叔丁基过氧化氢。

脱模剂：硬脂酸锌，硬脂酸铅，脂肪酸酰胺，有机硅油；

着色剂：钛白、油性黑、大分子系颜料铁红。

上述原料配好后，将其在低于所用引发剂半衰期为10小时分解温度

２０℃以下的温度范围内并按表三规定的工艺条件和图工特种不饱和聚酯模塑料制造工艺流程图进行制造

本发明的有益效果：

本发明制造的特种不饱和聚酯模塑料，具有以往的不饱和聚酯模塑料所没有的下述令人惊叹的特性：

１、颗粒状原料大小相近，几乎无粉末存在，颗粒互不粘连，板状料为固态板料。

２、贮藏稳定性达１５个月以上（２４℃）

３、注塑成型（螺杆）加工性能优异，颗粒在料斗中下料流畅，并可模压或传递成型加工。

４、化学性能极稳定，耐酸、碱、油脂、及溶剂性能高于现有不饱和聚酯模塑料。

５、耐电弧性优（＞180-280秒），介电强度高，电绝缘性能优。

６、热传导率低，耐热湿度高，使用寿命长。

７、具有良好的耐辐射能力

８、比重较轻（0.8-1.8g/cm³），机械强度优良

９、价格低廉，性能优异，

本发明之特种不饱和聚酯模塑料，所具有的特殊性能，使得其系列产品可在航天、航空、汽车、船舶、机电设备等领域作绝缘材料，保温防火材料、防辐射、耐磨庶蔽材料，灭弧罩结构件、壳体等，具有优异的节能效果。

实施例１：

１，４－丁醇（BD），对苯二甲酸二甲酯（DMT）顺丁烯二酸酐（MA），按BD：DMT：MA为２.２：１：２的摩尔比，先将BD

和DMT按配比量在间歇或连续反应釜中于１６０－２１０℃进行酯交换反应，馏出副产物甲醇和四氢呋喃，当它们馏出量达到理论量的86-90%时，停止反应，将生成物对苯二甲酸双羟丁基酯泵入装有按配比量称取的MA的缩聚反应釜中，于１８０－２１０℃釜温、反应器顶温度160-190℃下，在N_2气保护下反应1.5-2.5hr，然后加入反应物重量面分比0.002% 的阻聚剂对苯二酚，于210-250℃，133Pa压力下反应4-6hr，降温至230℃以下，真空施压7-10kPa，反应0.8-1.2hr，接着降至4-7KPa，反应0.4-0.8hr，然后降至1-4KPa，反应0.2-0.6hr，最后降至0.1-1KPa，反应0.1- 0. 5hr 酸值达到15mgKOH/g后在200℃温度以下将熔融的UP卸出，冷却，即得本发明所用的结晶全固态UP树脂，反应过程中，蒸出的BD和少量的四氢呋喃，由回收系统回收。

将上述制好的UP与０－１０%的滑石粉掺混，粉碎成0.1-1000um的粉料，按表4所列的各例配方，采用德国LEISTRIT2公司ZSE 系列双螺杆行星齿混炼挤出造粒机组或类似的双螺杆挤出造粒机组，在105℃<温度范围内，进行混合、混炼，上丝挤出热切粒即得本发明的特种不饱和聚酯模塑料的颗粒料。

实施例２：

PTA：EG：MA按１：２.１：２的摩尔比进行计量，采用连续聚酯化缩聚的方法制UP树脂，其反应的工艺条件见表５

按上述条件制得的UP树脂连续不断的送去板状料制造生产线，制成板状固态纤维布模塑料。

上述制得UP树脂，也可连续不断的送去冷却粉碎制0.1-1000um粉粒，然后将UP树脂粉采用实施例1的方法进行造粒。

实施例３：

UP树脂粉分别按实施例１或２的方法制造，将UP树脂粉分别配以

表３所列各实施例配方进行称量，首先将粉状和液态助剂和改性材料加入高速混合机中，在＜８０℃温度以下，混合２－５分钟后加入无碱玻璃短纤维混合２－５分钟，将混合好的物料加入螺旋间歇定量加料器中，螺旋加料器定时定量加入双辊混炼机中，在９０－１００℃混炼８－１０分钟，然后出料，将带状料制成板状料或通过切料机制成方块粒料。

实施例４：

取上述实施例所制的颗粒料于热固注射成型机制样，注塑工艺参数为：

料筒温度：４０－７０℃（加料则）７０－９５℃（喷嘴侧）

模具温度：１７０－２２０℃

注射压力：５－８MPa

背　　压：0.5-1MPa

螺杆转速：６０－８０转/分

时　　间：注塑成型１－５min 脱模后于180-250℃熟化0.2-20hr

按GB1141-78　测试样耐电弧性为180-280秒

按GB1140-78　测其绝缘电阻：绝缘电阻为10^{9}-10^{17}(Ω)

按GB1636-79　测试样密度：密度为0.8-1.8g/cm^{3}

燃烧性：　　UL94 V-0级

按GB1634-79　测试样热变形温度≥200℃

图一 特种不饱和聚酯模塑料制造工艺流程图

图二 固态对苯二甲酯型UP树脂制造工艺线路图

图三 特种不饱和聚酯模塑料制造工艺流程图

表一

制造方法	原料配比 摩尔比	催化剂	阻聚剂	反应物	反应条件 温度 (℃)	时间 hr	压力 KPa	设备条件	其它条件	UP 酸值 koHmg/g
间歇酯交换缩聚法	DMT:EG (BD): MA 0. 4-0. 7: 0. 9--1. 6: 0. 8-1. 5	0 — 0.2	0.0005—0.1	DMT+EG (BD)	160-220	3-6		酯交换反应器		25<
				+MA	190-260 200-280	5-8 2-5	0. 1-2 0.1-2.0	缩聚反应器	输入氮气、加对苯二酚	
间歇酯化缩聚法	PTA: EG : MA 0. 9-1. 2: 1. 4-2. 4: 1. 3-2. 4			PTA EG	180-240	3-6		酯化反应器		
				+ MA	200-250 210-280	4-7 3-6	0. 1-3 0.1-2.5	缩聚反应器	输入氮气 加对苯二酚	
连续酯交换缩聚法.	DMT:EG (BD):MA 0. 4-0. 7: 0. 8-1. 2: 0. 8-1. 5			DMT+EG (BD)	160-230	1.5-3.5		第一酯交换反应器		
					180-240	1.5-3.5		第二酯交化反应器		
				+MA	180-220	1.5-3.5	0. 133	第一缩聚反应器	输入氮气	
					190-260	1.5-3.5	0. 3-3	第二缩聚反应器	加对苯二酚、	
					200-280	1.5-3.5	1. 5-11	第三缩聚反应器		
					210-280	1.5-3.5	0.1-1. 5	第四缩聚反应器		
连续酯化缩聚法	PTA : EG MA 0. 9-1. 3: 1-2. 6: 1. 3-2. 5			PTA+EG:	180-240	1.3-3.8		第一酯化反应器		
					190-260	1.3-3.8		第二酯化反应器	输入氮气	
				+MA	180-220	1.3-3.8	0. 133	第一缩聚反应器	加对苯二酚	
					200-280	1.3-3.8	0.5-3. 5	第二缩聚反应器		
					200-250	1.3-3.8	2-10	第三缩聚反应器		
					210-280	1.3-3.8	0.1-1. 5	第四缩聚反应器		

表二 特种不饱和聚酯模塑料的原材料配比

原料名称	材料性状	份量 重量百分比（%）
UP树脂	0.1um-1000um结晶细粉	10-70
引发剂	细晶粒用二甲苯甲苯调配与交联剂混溶	0.01-5
交联剂	粉状	0.1 -10
填充剂	细粉粒径≤500um	0-75
增强材料	长纤维短纤维纤维布网含Pb含金钢丝 ϕ <0.10mm	5-70
改性材料	细粉	0-60
阻燃剂	稠状液体；细粉	0-60
脱模剂	细粉,	0.1-3
着色剂	粉状≥500目	0.001-0.1

表三 特种不饱和聚酯模塑料制造工艺条件

设备条件	制造顺序	控制要点		模塑料性状
		温度 ℃	时间 min	
ZSE 系列挤出造粒生产线气动混合器 折流板双锥混合机 高速混合机、振动筛 混炼装置、挤出机 切粒机、螺旋加料器	原料计量——混合——混炼——上丝——排气——挤出—机头—热切料／冷条切——过筛——计量—包装	40-80 70-99	2-5 5-8	颗粒状 固态
平板模塑料生产线	UP树脂粉—传送带—板块料生产线；纤维布—板块料生产线；—固态平板料	105<	12<	板状 固态
高速混合机 螺旋加料器 密炼机 振动筛 两辊机 切粒机	计量——混合——加料—塑炼 密炼——两辊机引条——上长纤维—固态平板料；—造粒—过筛—包装	80—150	6-8	固态

表四

	实施例								
	1	2	3	4	5	6	7	8	9
UP树脂	25	25	20	23	30	28	15	32	18
马来酰亚胺	3		4				5		
M型单体		4				6			
聚胺一酰胺酸				1.5	2			2	0.5
过氧化二异丙苯	0.5			0.4	0.6				
枯基过氧化氢		05	0.8			1	1	0.2	
中空玻璃微球	40	20	20	30	50	30	20		35
轻质碳酸钙		10	13	35		8		20	10
滑石粉	0.5								
聚三氟氯乙烯纤维			2						3
无碱玻璃纤维	9	10	12	6	15	14	10	25	12
氢氧化铝	10	10	15				12		6
四溴双酚A				3.5					
氟塑料40	11	20					9	20	
三聚氰胺甲醛模塑粉									15
脂肪酸酰胺	1	0.5	1.2	0.6	1	1	2	0.8	0.5
聚双马来酰亚胺			10			10	26		
聚酰亚胺纤维			2		1.4	2			

表 5

		反应条件			其它条件
		时间hr	温度(℃)	压力KPa	
缩聚反应器	第一酯化反应器	1.5-3.5	180-200	0.3-3	
	第二酯化反应器	1.5-3.5	180-240	0.1 2.5	
酯化反应器	第一缩聚反应器	1.3-2.4	200 220	0.133	输入氮气
	第二缩聚反应器	1.3-2.5	210-280	0.5-3.5	对苯二酚
	第三缩聚反应器	1.4-2.4	220 240	1.5-11	
	第四缩聚反应器	1.3-3.8	190-260	0.1-3	

说 明 书 附 图

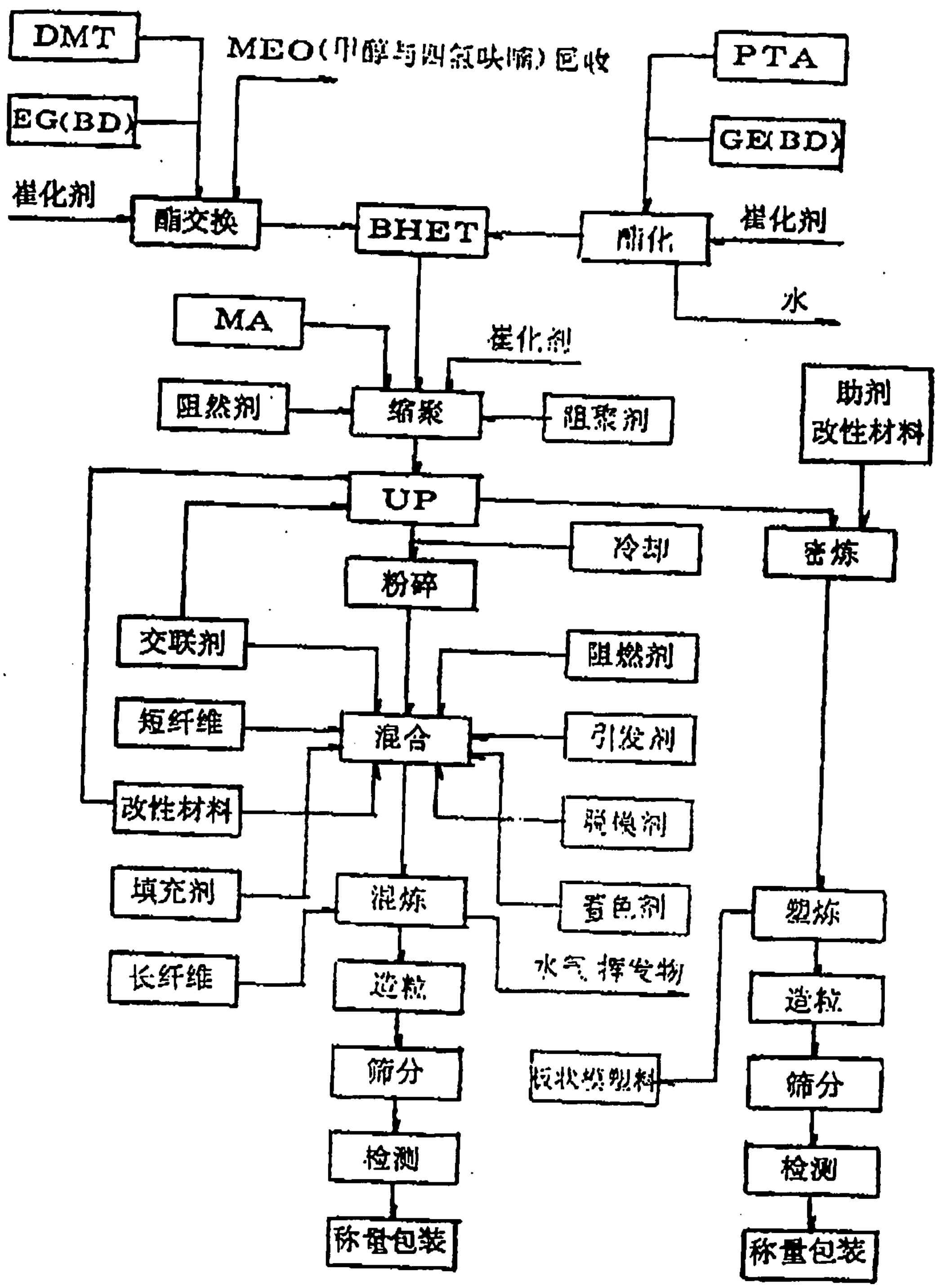
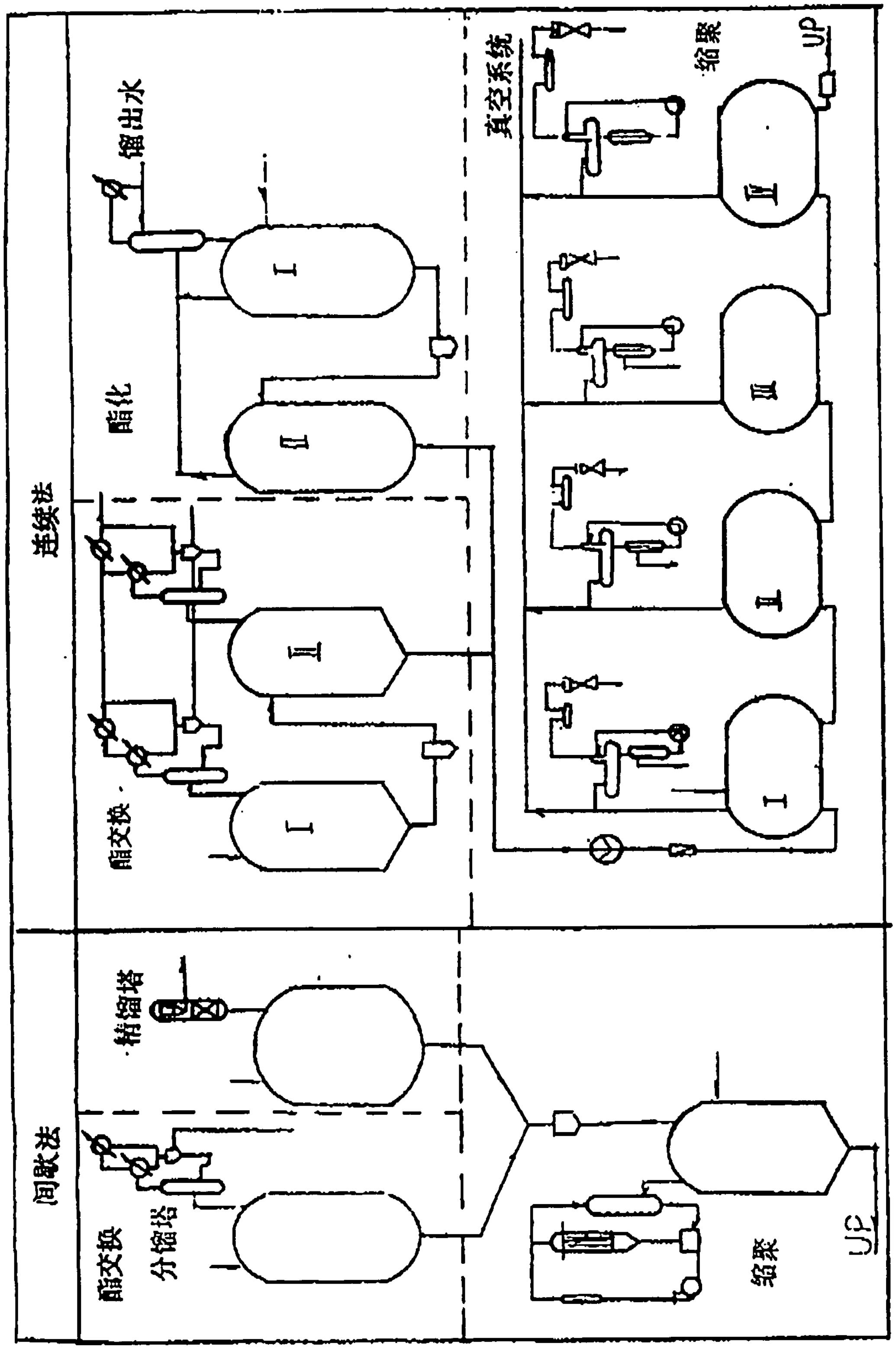
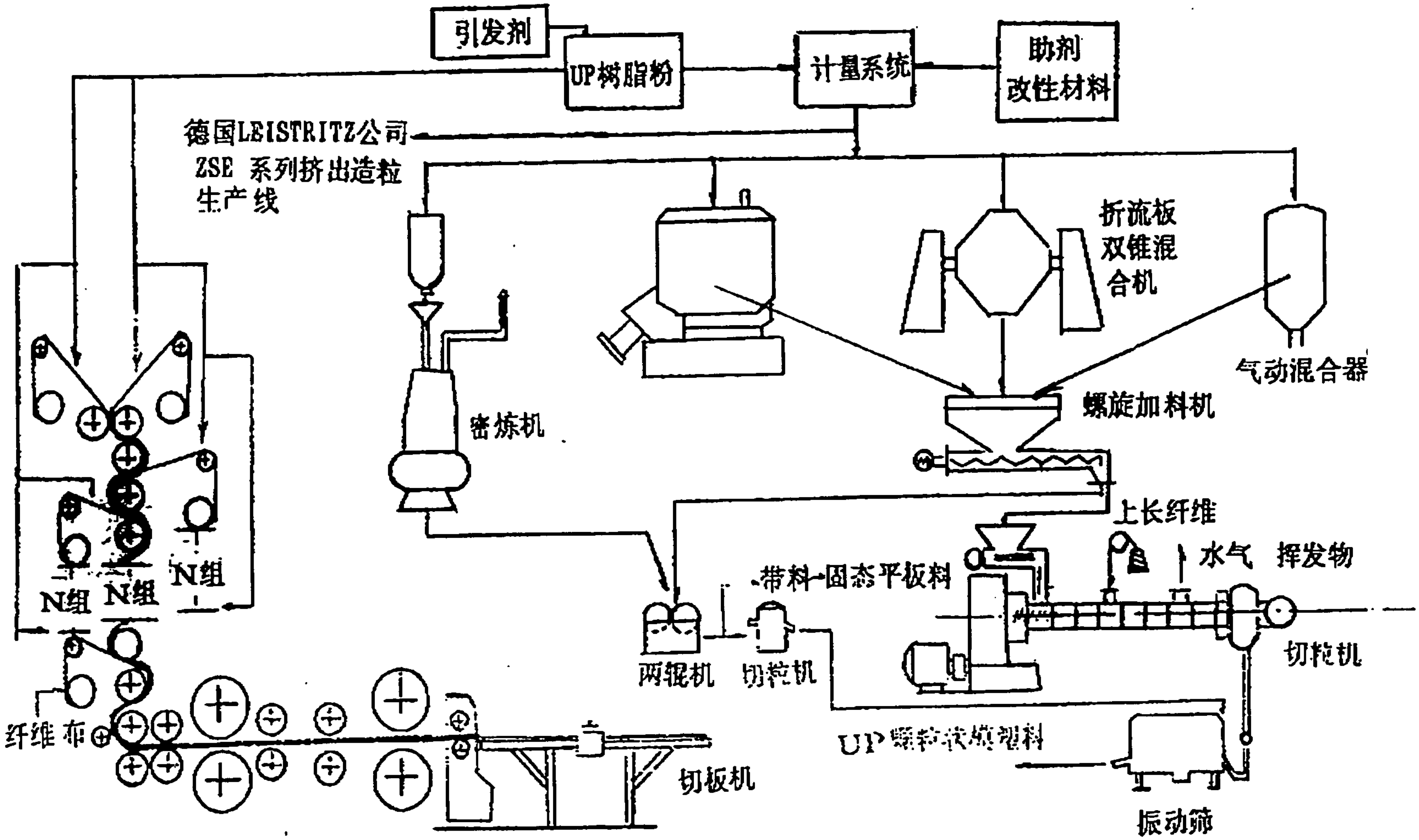

DMT
EG(BD)
MEO(甲醇与四氢呋喃)回收
PTA
GE(BD)
催化剂
酯交换
BHET
酯化
催化剂
水
MA
催化剂
阻燃剂
缩聚
阻聚剂
助剂
改性材料
UP
冷却
密炼
粉碎
交联剂
阻燃剂
短纤维
混合
引发剂
改性材料
脱模剂
填充剂
混炼
着色剂
塑炼
长纤维
造粒
水气挥发物
造粒
筛分
板状模塑料
筛分
检测
检测
称量包装
称量包装

图 1



图二



纤维布板块模塑料生产线

图三